

CARBON MONOXIDE-WATER vs. HYDROGEN FOR LIQUEFACTION:
THE REDUCTION OF DIPHENYLSULFIDE, THIOANISOLE AND DIBENZOTHIOPHENE

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INTRODUCTION

For lignite, several workers have demonstrated a mixture of carbon monoxide and water to be superior to hydrogen for liquefaction when there are no added catalysts(1, 2, 3, 4). The minerals present in lignite are postulated to catalyze the reduction. The relative success of CO is important because it suggests the economics of lignite liquefaction may ultimately favor the use of synthesis gas over hydrogen. If so, the need of the shift reaction section of a hydrogen plant can be eliminated. Carbon dioxide has to be removed at one stage in either process which will probably result in a wash-out of its removal expenses.

There are several important questions which arise from the carbon monoxide results: (1) Which chemical bonds are more easily reduced by CO-H₂O than H₂ under the same conditions? (2) Does the reduction proceed because of "nascent" hydrogen from CO-H₂O? and (3) What materials catalyze the CO-H₂O reaction?

Model compounds are superior to lignite as a material to study to answer the posed questions because the variables can be better controlled. The applicability of the model compound work to lignite liquefaction processes depend upon the relation of the model compounds to the key features of lignite structure and chemistry question examined. The selection of the materials for examination as catalysts depends on the nature of the natural minerals present in the various lignites, available low-cost materials as disposable catalysts and materials to prove or disprove a hypothesis on catalyst activity.

Carbon monoxide and water has proven more effective than hydrogen to convert benzophenone and benzhydrol into products(5). For anthracene, H₂ and CO-H₂O are equally effective for conversion, and for quinoline H₂ is superior to CO-H₂O(6). The product distributions are influenced by catalysts and the presence of a hydrogen-donor solvent.

Thiophene and thiophene derivatives have been desulfurized by tetralin(7), hydrogen over a CoO-MoO₃-Al₂O₃ catalyst(8), an ammonium Y zeolite catalyst(9) and a molybdenum sulfide catalyst(10). Rollman has removed sulfur from model compounds over sulfided CoMo catalysts(11).

EXPERIMENTAL

The reductions are done in a pair of 250-ml rocking Hastelloy C autoclaves. The temperature is maintained at 425°C for two hours. The heat up time is slightly more than an hour, and the cool-down time is done overnight. Initially the autoclaves are charged with 750 psi of reducing gases and 750 psi of argon (1500 psi total). At 425°C, the reactions will achieve a total pressure of about

3,000 psi. After cool-down, the gases are vented and the products removed by decanting.

The water layer is separated from the organic layer by a separatory funnel and filtered through a sintered glass funnel. A 3-ml aliquot of the resultant solution is combined with an appropriate internal standard and analyzed by gas-liquid chromatography. The results were obtained on a Varian Aerograph 90-P instrument and are duplicated with the precision of $\pm 6\%$.

RESULTS AND DISCUSSION

In the absence of possible catalysts, the effectiveness of the reducing gases is $H_2 \approx H_2 - CO - H_2O > CO - H_2O$ for causing conversion of diphenylsulfide (Table 1, runs 1-4) and thioanisole (Table 3, runs 2-4). Hydrogen, with or without carbon monoxide, causes predominantly transformation into benzene, whereas carbon monoxide-water gives a variety of products. The combination of hydrogen with carbon monoxide and water provide results intermediate in percentage yields.

In the absence of reducing gases, neither dibenzothiophene nor diphenylsulfide decompose at 425°C (Tables 1 and 2). However, thioanisole readily decomposes to give diphenylsulfide, toluene and benzene (run 1 of Table 3). Since the latter reaction solution is essentially nonpolar, homolysis of the sulfur-methyl bond is most probably occurring, i.e., reaction 1. The dissociation energy of this bond is 60 kcal/mole¹². Little thiophenol is formed possibly because of the low S-H bond energy. Reactions 2^c and 3 are likely reactions to account for the benzene formed. Reaction 4 illustrates the reaction route to the predominant product, diphenylsulfide. Reaction 5 outlines a possible reaction route to toluene.

For the three sulfur compounds of Tables 1-3, hydrogen is superior to carbon monoxide-water for desulfurization. The CO-H₂O results can be accounted for by the reduction caused by hydrogen from the shift reaction, reaction 6, rather than an interpretation wherein CO directly reacts with the three model compounds.

Since benzoic acid is formed in the reactions of diphenylsulfide and thioanisole only when carbon monoxide is present, it must be the source of the carboxyl group directly or indirectly. The sequence of reactions 7 and 8 are probable for the formation of benzoic acid under these high pressure conditions.

- 1) $Ph-S-CH_3 \rightarrow Ph-S + CH_3$
- 2) $Ph-S \rightarrow Ph + S^{013}$
- 3) $Ph + PhSCH_3^* \rightarrow PhH + PhSCH_3$
- 4) $Ph + PhSCH_3 \rightarrow PhSPh + CH_3$
- 5) $PhSCH_3 + CH_3 \rightarrow PhCH_3 + SCH_3$
- 6) $CO + H_2O \rightleftharpoons CO_2 + H_2$
- 7) $Ph + CO_2 \rightarrow PhCO_2$
- 8) $PhCO_2 + PhSCH_3^* \rightarrow PhCO_2H + PhSCH_2$

(* or metal -H)

In the diphenylsulfide reductions results described in Table 3, carbon monoxide must be the source of the methyl group of toluene. In support of this, the phenyl ring is unlikely to fragment to a methyl group under these conditions for thermodynamic reasons, and no toluene is formed when hydrogen is used as the sole reducing gas.

The added materials, tetralin, Na_2CO_3 and FeS , inhibit the diphenylsulfide and thioanisole reduction conversions and have little net effect on the dibenzothiophene reactions. Tetralin is not behaving as a good hydrogen donor, but rather as an inert diluent of the reducing gases. Less than 5% of the tetralin is converted into naphthalene.

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Table 1. Reduction of Diphenyl sulfide¹

Run	Reducing gases ²	Solvent	Catalyst ³	Benzene, % ⁴	Toluene, % ⁴	Thiophenol, % ⁴	Thioanisole, % ⁴	Benzoic acid, % ⁴	Conversion, % ⁵
1	None	None	None	2.3	0.0	0.0	0.0	0.0	2.3
2	CO-H ₂ O	None	None	31.0	2.4	4.3	0.0	26.7	64.4
3	H ₂	None	None	100.0	0.0	0.0	0.0	0.0	100.0
4	CO-H ₂ O, H ₂	None	None	91.4	4.0	0.0	0.0	3.8	99.2
5	CO-H ₂ O	None	Na ₂ CO ₃	11.8	0.7	4.0	0.4	30.4	47.3
6	H ₂	None	Na ₂ CO ₃	53.7	0.0	0.0	0.0	0.0	53.7
7	CO-H ₂ O, H ₂	None	Na ₂ CO ₃	41.4	0.5	0.4	0.0	1.1	43.4
8	CO-H ₂ O, H ₂	Tetralin	Na ₂ CO ₃	18.1	0.2	0.0	0.0	0.0	18.3
9	CO-H ₂ O, H ₂	None	FeS	52.1	2.2	3.0	trace	11.1	68.4

1. 0.15 mole total.

2. Each gas is at 750 psi initial pressure except when hydrogen and carbon monoxide are used simultaneously; then each is at 375 psi initial pressure. Argon is added to bring the total pressure to 1500 psi.

3. 0.015 mole.

4. Normalized to converted starting material.

5. Based on recovered starting material.

Table 2: Reduction of Dibenzothiophene¹

<u>Run</u>	<u>Reducing gases</u>	<u>Catalyst</u>	<u>Solvent</u>	<u>Diphenyl, %</u>	<u>Conversion, %</u>
1	H ₂ , H ₂ O	None	None	2.7	2.7
2	H ₂ , H ₂ O	Na ₂ CO ₃	None	0.6	0.6
3	CO, H ₂ O	Na ₂ CO ₃	None	1.2	1.2
4	H ₂ , CO, H ₂ O	Na ₂ CO ₃	None	0.8	0.8
5	H ₂ , CO, H ₂ O	Na ₂ CO ₃	Tetralin	2.3	2.3
6	H ₂ , CO, H ₂ O	FeS	None	1.7	1.7

1. 0.15 mole and the footnotes of Table 1 apply here also.

Table 3. Reduction of Thioanisole¹

Run	Reducing gases ²	Solvent	Catalyst ³	Benzene, % ⁴	Toluene, % ⁴	Diphenyl sulfide, % ⁴	Thiophenol, % ⁴	Benzoic acid, % ⁴	Conversion, % ⁵
1	None, H ₂ O ⁶	None	None	4.4	29.5	38.2	1.4	0.0	80.7
2	H ₂ , H ₂ O	None	None	84.1	1.1	0.0	0.0	0.0	85.2
3	CO, H ₂ O	None	None	10.9	6.9	9.5	0.4	12.8	40.5
4	H ₂ CO, H ₂ O	None	None	76.1	5.7	1.8	trace	2.5	86.1
5	H ₂ , H ₂ O	None	Na ₂ CO ₃	37.7	4.3	1.4	0.0	0.0	43.4
6	CO, H ₂ O	None	Na ₂ CO ₃	24.5	10.0	7.0	trace	1.9	43.4
7	H ₂ , CO, H ₂ O	None	Na ₂ CO ₃	14.0	7.3	3.0	0.0	0.0	24.3
8	H ₂ , CO, H ₂ O	Tetralin ³	Na ₂ CO ₃	9.3	0.9	1.2	0.0	0.0	11.4
9	CO, H ₂ O	None	FeS	14.9	7.8	8.9	0.0	17.8	49.4
10	H ₂ , CO, H ₂ O	None	FeS	32.7	8.0	4.5	8.5	8.1	61.8
11	CO	None	None	2.7	44.8	15.8	0.0	-	63.3

1. 0.15 mole.

2. Each gas is at 750 psi initial pressure except when hydrogen and carbon monoxide are used simultaneously; then each is at 375 psi initial pressure. Argon is added to bring the total pressure to 1500 psi.

3. 0.015 mole.

4. Normalized to converted starting material.

5. Based on recovered starting material.

6. Contains 7.2% of an unidentified material.